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Supplementary materials for:

Complexation ability of octaazamacrocyclic ligand towards Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} Metal cations; Experimental and theoretical study

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CSD search

Structures of transition first row metal/*tpmc* complexes fined in crystallographic data bank (CSD) can be divided in three different sets based on differences in geometry (Table 1-S).

In all found complexes, each metal ion is *exo* coordinated by two nitrogen atoms separated with two CH_2 groups from *tpmc* ring (NCH_2CH_2N group) and two nitrogen atoms from 2-pyridylmethyl pendant groups. In the 11 of extracted structures transition metal atom is pentacoordinated with different ligands occupying fifth coordination site. One structure (OGAMEP) contains hexacoordinated Co(II) ions with bidentate NO_3^- ligand on fifth and sixth coordination site.

Table 1-S. Molecular symmetry and geometrical parameters of reported first row transition metal/*tpmc* complexes recorded in CSD.

CSD refcode	Complex	Symmetry group of complex ion	Symmetry group of *tpmc* ring	*Tpmc* ring conformation	τ	Ref. in a paper
			A set			
DUJKEY	$[Cu_2(Br)_2tpmc](ClO_4)_2$	*Ci*	*Ci*	chair	0.7	[30]
OGAMEP	$[Co_2(tmpc)(NO_3)_2][NO_3]_2 \cdot MeOH$	*Ci*	*Ci*	chair	0.65	[31]
OGAMIT	$[Co_2(tmpc)Cl_2]^{2+}$	*Ci*	*Ci*	chair	0.835	[31]
YEXHIT	$[Co_2(Cl)_2tpmc](BF_4)_2$	*Ci*	*Ci*	chair	0.68	[32]
			Symmetric B set			
VEGKOH	$[Cu_2OH(tpmc)](ClO_4)_3 \cdot 2H_2O$	*Cs*	*Cs*	boat	0.58	[33]
VEPPUB	$[Cu_2(F)tpmc](ClO_4)_3 \cdot 2CH_3CN$	*Cs*	*Cs*	boat	0.33, 0.09	[34]
VEPRAJ	$[Cu_2(Cl)tpmc](ClO_4)_3 \cdot H_2O$	*Cs*	*Cs*	boat	0.31	[34]
			Nonsymmetric B set			
GAMYAV	$[Cu_2(tpmc)(\mu\text{-}CO_3)](BPh_4)_2$	*C1*	*Cs*	boat	0.29, 0.05	[35]
GIPGES	$[Cu_4(succinato)(tpmc)_2](ClO_4)_6 \cdot 2C_2H_5OH \cdot 4H_2O$	*C1*	*Cs*	boat	0.40, 0.05	[36]
GIPGIW	$[Cu_2(C_6H_5COO)tpmc](ClO_4)_3 \cdot 0.5CH_3OH \cdot 0.5H_2O$	*C1*	*Cs*	boat	0.79, 0.09	[36]
VEGKUN	$[Cu_2NO_3(tpmc)](PF_6)_3$	*C1*	*Cs*	boat	0.29, 0.02	[33]
XUBNOX	$[Cu_2(HCOO)tpmc](ClO_4)_6 \cdot 6H_2O$ $[Cu_2(CH_3COO)tpmc]^{3+}$	*C1*	*Cs*	boat	0.28, 0.16 0.38, 0.02	[37]

All the structures classified as A set contain center of inversion in the middle of the complex. Complex consists of two separated independent metal binding sites with metal atoms far apart (around 5.7 Å). Geometry of the metal binding site is close to trigonal-bipyramidal as indicated with high values of τ parameters. Nitrogen atoms from *tpmc* ligand occupy both axial and two equatorial positions in all A set structures. Chloro ligand is bound to the third equatorial position in DUJKEY, OGAMIT and YEXHIT structures. In OGAMEP structure last coordination place is occupied by bidentate NO_3^- ligand with very small O-Co-O angle (57.1°) and this structure cannot be represented as distorted octahedral. If two oxygen atoms from NO_3^- ligand are represented as one ligating atom occupying the midpoint between those two atoms then the coordination geometry around Co^{2+} ion is destorted trigonal-bipyramidal with τ parameter of 0.65 (Fig 1-S).

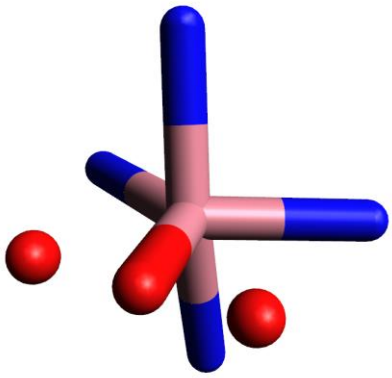

Figure 1-S. Coordination geometry about Co^{2+} ion in OGAMEP structure. Blue-pink sticks – Co-N bonds; red spheres – oxygen atoms from NO_3^- ligand; red-pink sticks – bond between Co^{2+} ion and midpoint of two oxygen atoms from NO_3^- ligand.

All 14-membered macrocyclic *tpmc* ligand rings from the A set structures are in the same centrosymmetric *chair* conformation (Fig 2-S, a). When superimposed onto each other, RMS (root mean square) displacement between heavy atoms from 14-membered *tpmc* ligand rings from all the A set structures is less than 0.1 Å.

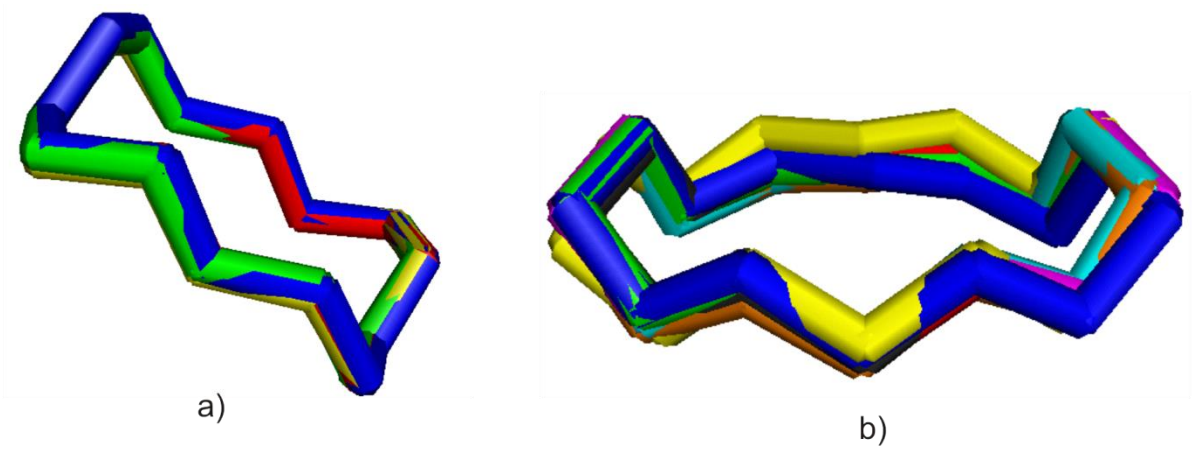

Figure 2-S. a) Superimposition of 14-membered *tpmc* ring heavy atoms from 4 structures consisting A set. b) Superimposition of 14-membered *tpmc* ring heavy atoms from 8 structures consisting B set.

All the structures classified as B set contain dinuclear Cu(II) *tpmc* complexes with additional bridging ligand connecting two Cu(II) ions. Common feature for all B set structures is that 14-membered *tpmc* ring is in the symmetric *boat* conformation (Cs symmetry point group) with mirror plane normal to the ring plane. RMS displacement between the *tpmc* ring atoms for B set structures is between 0.1 and 0.15 Å (Fig 2-S, b). Metal-metal distances in B set structures are much shorter than in A set structures, ranging from 3.7 to 4.6 Å.

In the three B set structures symmetric bridging ligand is monodentate ligand (OH^-, F^- and Cl^- ions) thus forcing the whole complex to adopt the mirror plane symmetry (symmetric B set). The mirror plane is defined with two midpoint carbon atoms from 14-membered *tpmc* ring and donating atom from bridging ligand. Based on the τ parameter geometry about Cu(II) ions is distorded square-pyramidal with four *tpmc* nitrogen atoms occupying in-plane positions and bridging ligand atom occupying apical position.

In the other five B set structures bridging ligand is bidentate ligand and complex molecule loses its symmetry (nonsimmetric B set). This implies existence of different geometries about two Cu(II) ions in complex molecule; one in distorted square-pyramidal (close to trigonal-bipyramidal) geometry (τ parameters between 0.28 and 0.79) with four nitrogen atoms from *tpmc* in in-plane position and bridging ligand in apical position and other in square-pyramidal geometry (τ parameters less than 0.1) with three nitrogen atoms from *tpmc* and bridging ligand atom in in-plane position and fourth *tpmc* nitrogen atom in apical position.

Literature search on this subject gave another crystal structure of $[Co_2(ox)$*tpmc*$](ClO_4)_2$ (data not deposited in CSD) [1-S]. In this structure complex is in the unsymmetric B set conformation with oxalato ligand bridging two Co(II) ions.

Interestingly, no crystal structure of Ni(II) and Zn(II) ions with *tpmc* ligand were recorded in CSD or in literature. Some experimental evidence, such as IR spectra and magnetic susceptibilities measurements on $[Ni_2Br_2($*tpmc*$)](ClO_4)_2$ complex strongly suggest that this compound will have A set based geometry [2-S].

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